ELECTROCHEMICAL ENERGY STORAGE WITH CARBON ONIONS

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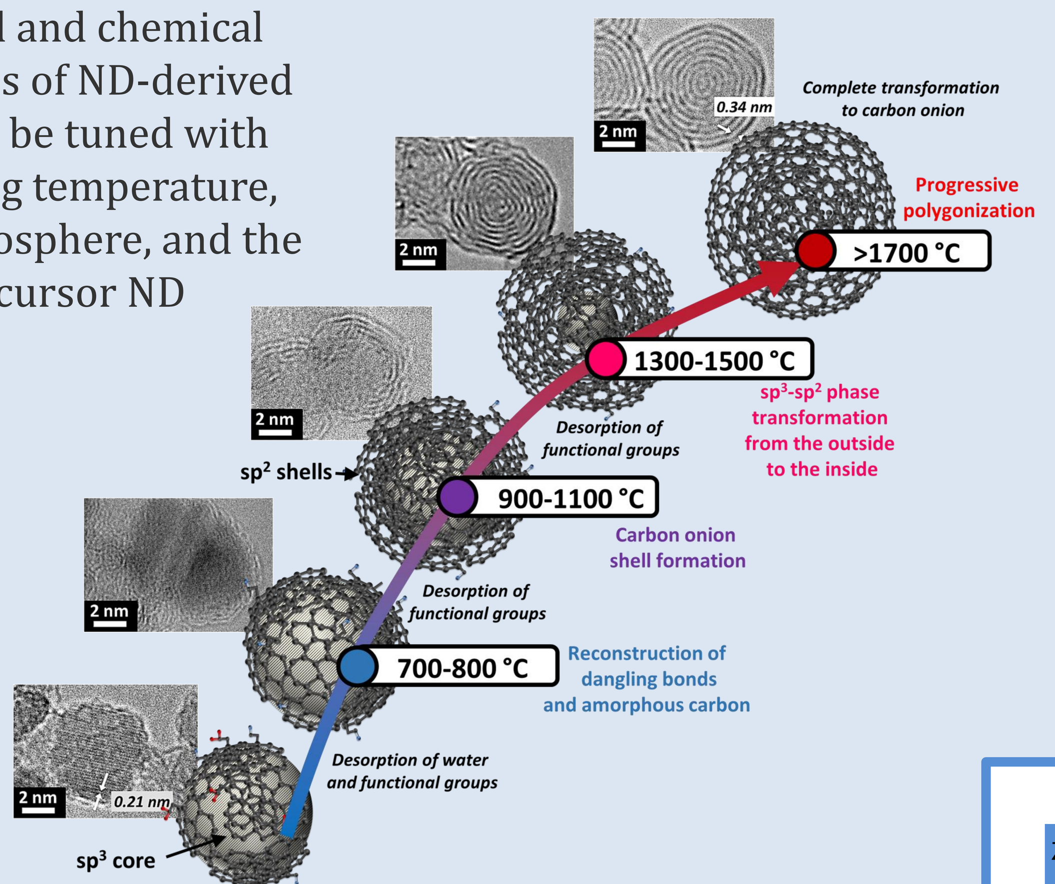
INTRODUCTION

Electric energy storage (EES) has emerged as an enabling technology for the widespread utilization of intermittent energy production from renewable energy sources. Electric double-layer capacitors (**supercapacitors**) have attracted particular attention because of their high power density and stable performance. A novel electrode material for supercapacitors is onion-like carbon (OLC). OLCs are spherical carbon nanoparticles consisting of graphitic onion shells with a diameter of 5-10 nm derived from nanodiamonds (ND) by thermal annealing. Compared to activated carbon (AC) with internal porosity carbon onions present only external surface area, which enables superior rate handling and loading with redox-active materials like metal oxides without blocking pores.

CARBON ONION SYNTHESIS FROM NANODIAMONDS

Phase transformation ND-OLC

Physical and chemical properties of ND-derived OLC can be tuned with annealing temperature, time, atmosphere, and the precursor ND

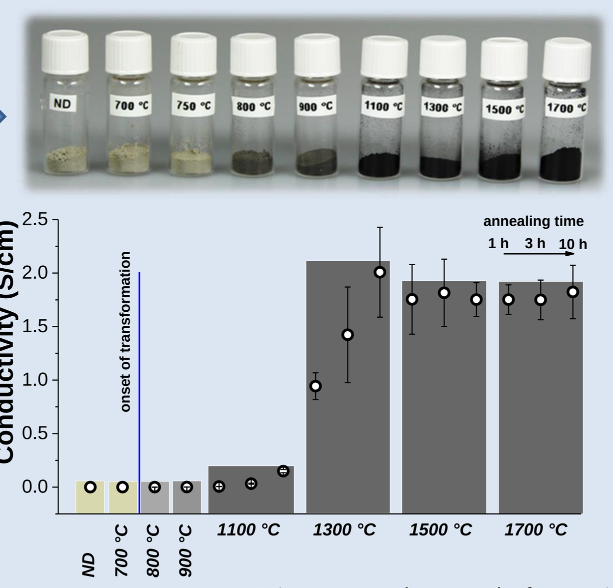


Zeiger M. et al, Journal of Materials Chemistry A. submitted

Zeiger M. et al., Carbon. 2015;84(0):584-98.

Conductivity

Increase in annealing temperature
→ **increase in DOS of conductive electrons**
→ **higher intrinsic conductivity**

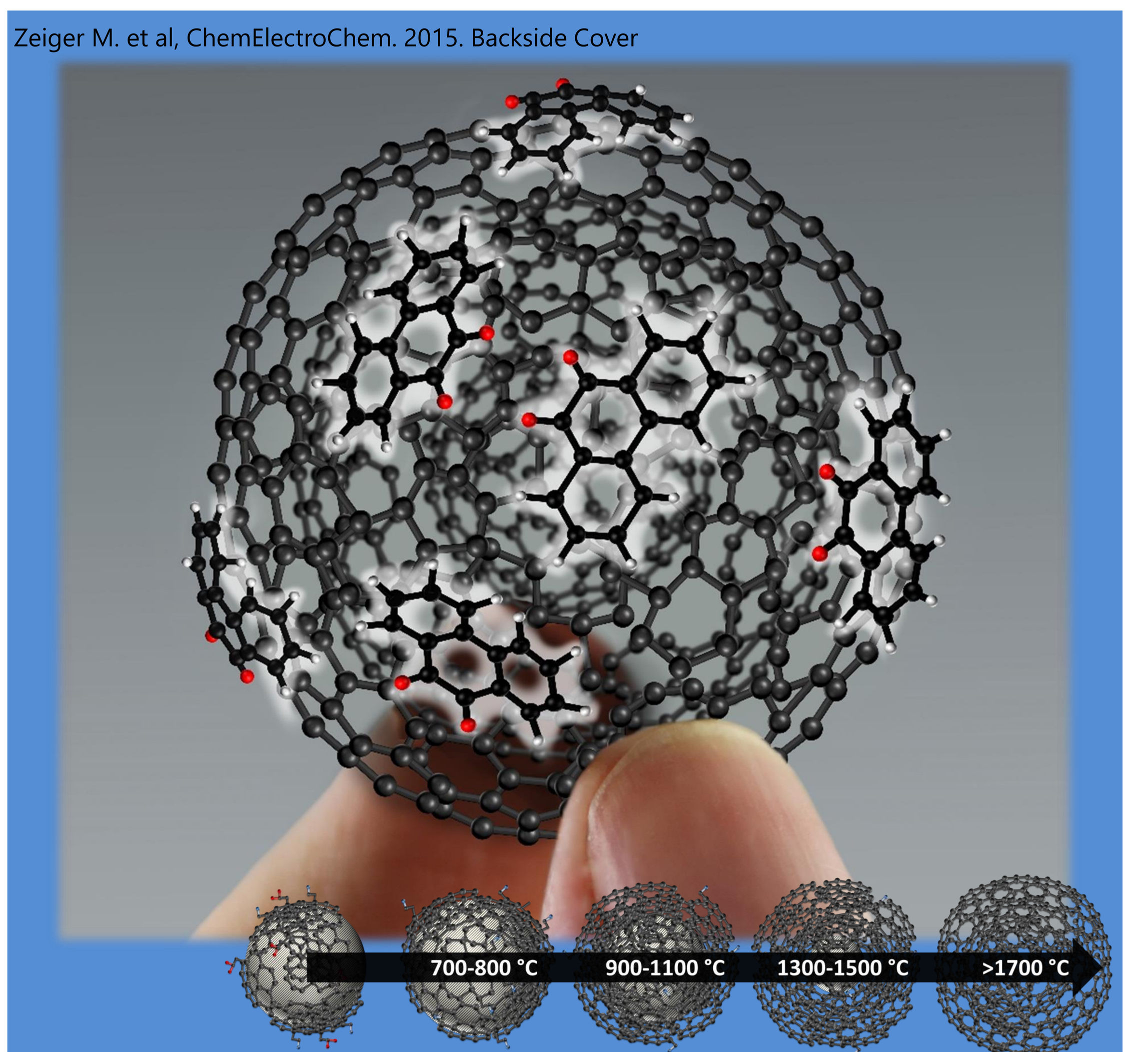


Controllable sp^2/sp^3 ratio

Conductivity measured on pellets using 4-point probe

Zeiger M. et al, Journal of Materials Chemistry A. submitted

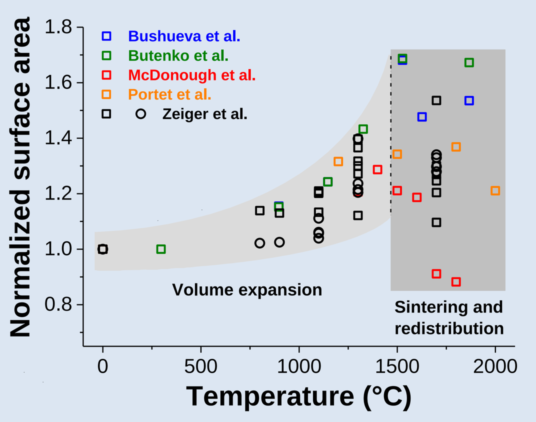
Zeiger M. et al, ChemElectroChem. 2015. Backside Cover



		700-800 °C	900-1100 °C	1300-1500 °C	>1700 °C
mass	100 %	95 %	92 %	90 %	88 %
oxygen content	5 %	4 %	4 %	3 %	1 %
ND content	>90 %	>90 %	>75 %	>40 %	0-5 %
density	3.3 g/cm³	2.9 g/cm³	2.5 g/cm³	2.2 g/cm³	1.9 g/cm³
surface area	280 m²/g	300 m²/g	350 m²/g	390 m²/g	420 m²/g
sp² carbon ordering	very low	low	low	medium	high
conductivity	~0 S/cm	0.25 S/cm	2 S/cm	2 S/cm	2-4 S/cm

Surface area

- During annealing the density decreases
  → **increase in particle volume**
  → **increase in surface area**
- The **increase is limited** by redistributed carbon to larger graphitic structures due to carbon etching by desorbing surface functional groups



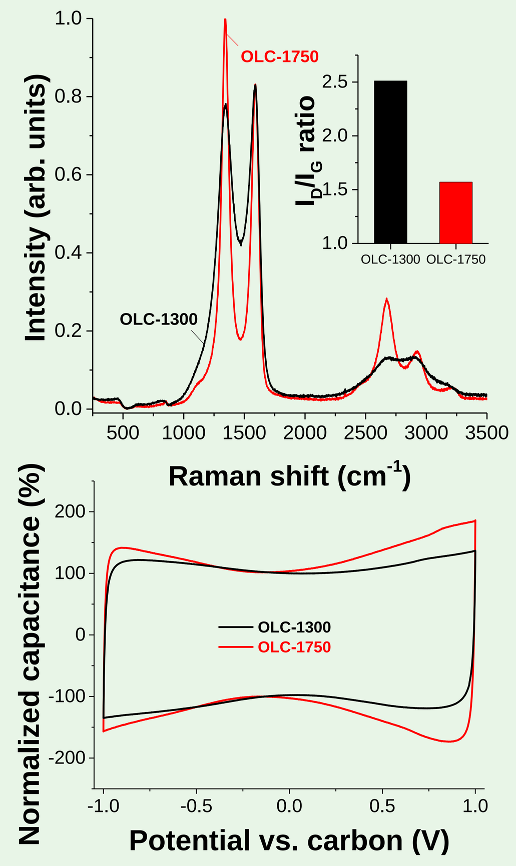
SSA_{ND}~280 m²/g
SSA_{OLC}~400 m²/g
SSA_{AC}~1500 m²/g

Surface area is measured using nitrogen gas sorption and normalized to the precursor

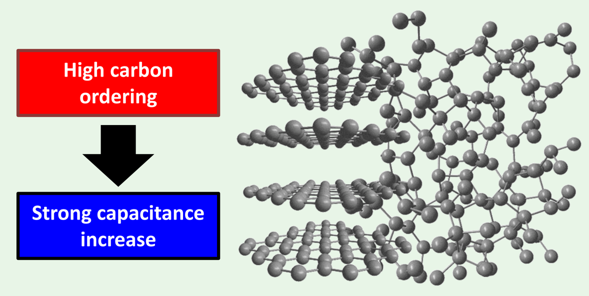
Zeiger M. et al, Journal of Materials Chemistry A. submitted

CARBON ONIONS FOR CAPACITIVE ENERGY STORAGE

Carbon onions as model material



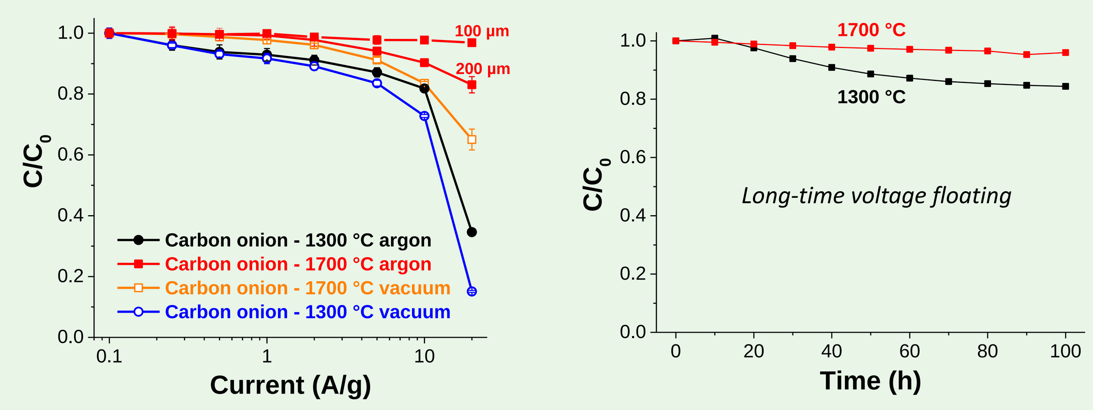
- Carbon ordering increases with annealing temperature



- Potential-dependent capacitance increases with carbon ordering

Weingarth D. et al. Advanced Energy Materials 4.13 (2014)

Carbon onions as electrode material



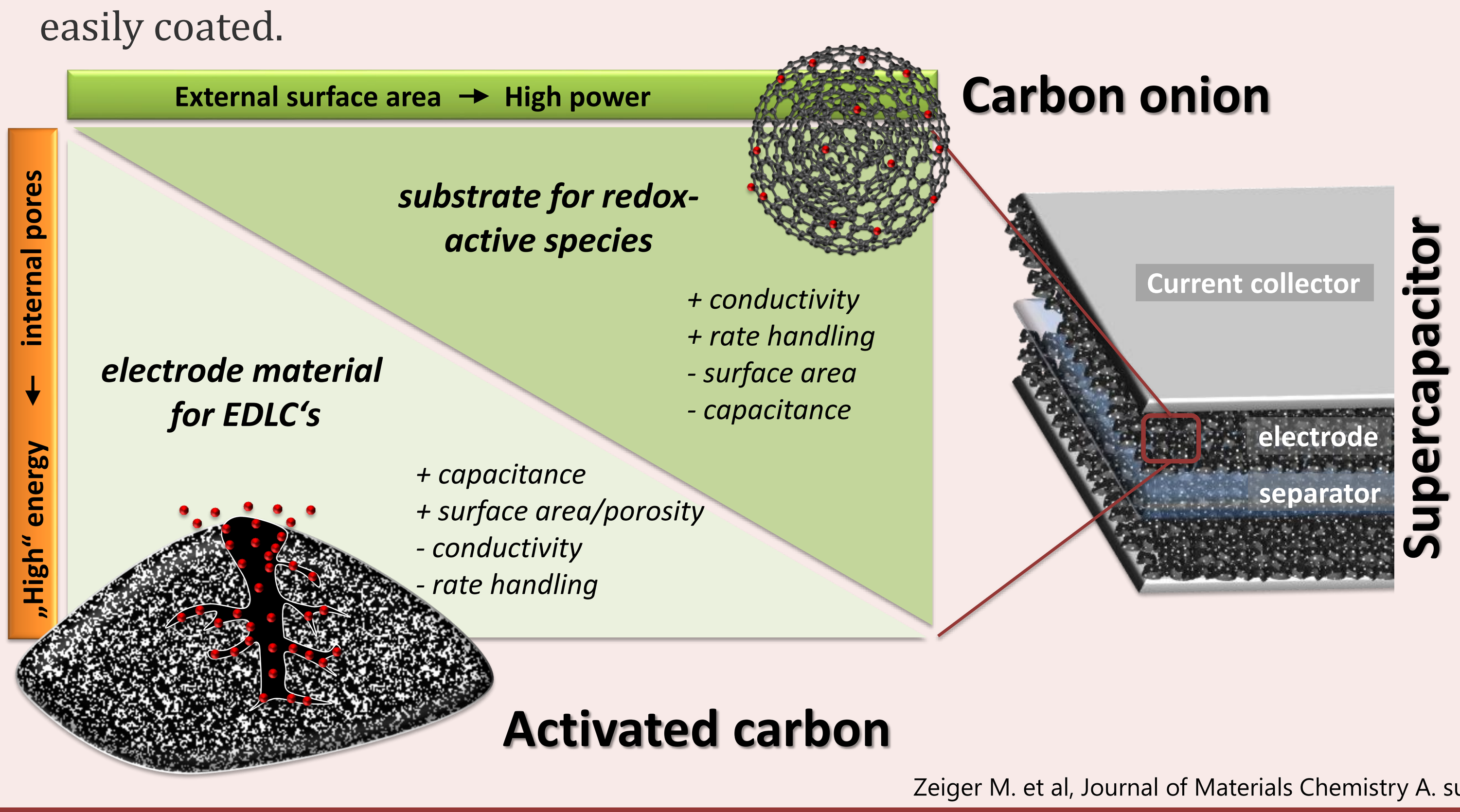
- **Capacitance: 20-40 F/g**
  (activated carbon: ~ 120 F/g)
- **Superior rate handling and high stability of high temperature carbon onions** (high degree of carbon ordering and less surface functional groups)
- Annealing in **argon** enhances rate handling due to formation of **few-layer graphene** as conductive additive

Zeiger M. et al., Carbon. 2015;94:507-17.

CARBON ONIONS FOR REDOX SYSTEMS

Material selection criteria

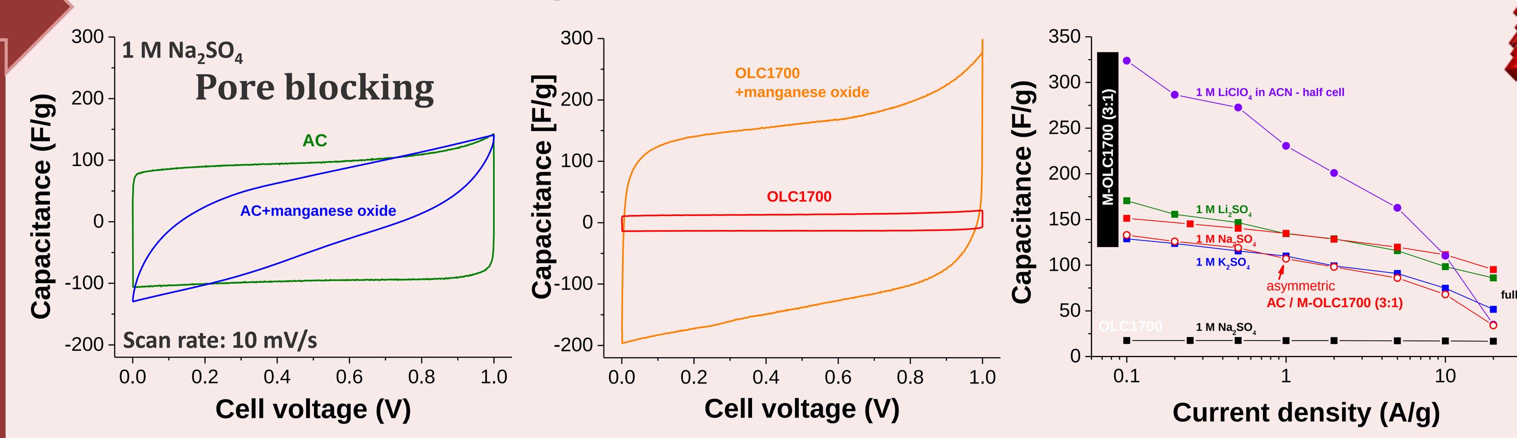
- The **energy density of EDLC's** can be significantly increased by loading the carbon material with **metal oxides, conducting polymers, or functional groups**.
- By coating AC, the standard material in EDLC's, with redox-active materials, pores are blocked and the composite suffers from the low conductivity of the AC
- Carbon onions, in contrast, present only external surface area, which can be easily coated.

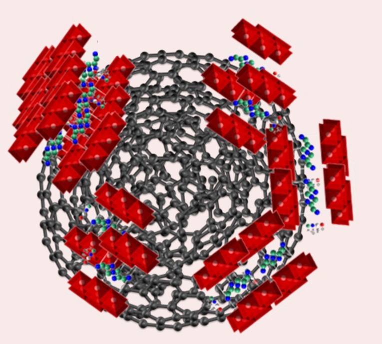


Zeiger M. et al, Journal of Materials Chemistry A. submitted

Carbon onion/manganese oxide hybrid electrodes

- Carbon onions and activated carbon are hydrothermally coated with birnessite using $KMnO_4$

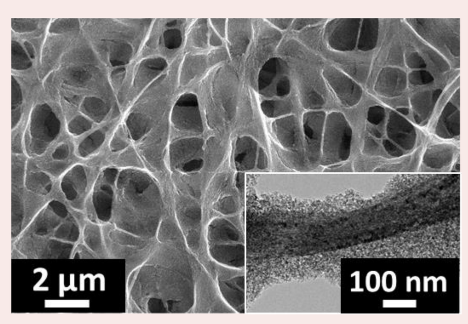


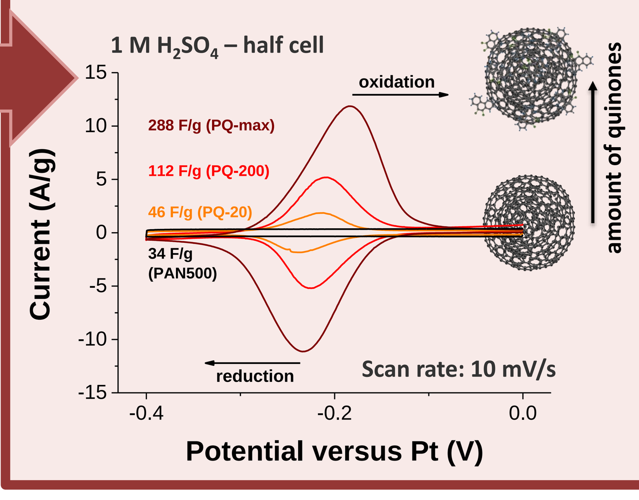


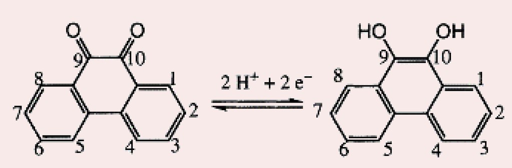
- **AC/birnessite** presents **high resistance** and **low capacitance** due to pore blocking
- **OLC/birnessite** shows **enhanced capacitance with good rate handling behavior**

Quinone-decorated carbon onion electrodes

- Synthesis of free-standing carbon onion/carbon fiber electrodes and functionalization with 9,10-phenanthrenequinones







- Capacitance increases with quinone-loading
- High capacitance of **288 F/g at 10 mV/s**
- **Excellent power handling** (> 100 F/g at 2 V/s scan rate)

Zeiger M. et al, ChemElectroChem. 2015.

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